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CALCIUM SILICATE CRYSTAL BOARD

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(57) Claim

1. A board of calcium silicate crystals, characterized in that the board is composed of a plurality of laminated thin sheets, each of the thin sheets having a thickness of 2 mm or less, containing secondary particles of calcium silicate crystals, a fibrous material and a coagulant adsorbed on the surface of the secondary particles, and being formed from the secondary particles interconnected with one another, and said superposed thin sheets being firmly united with one another into an integral body by the secondary particles of calcium silicate crystals present on the surface of the sheets.

8. A board of calcium silicate crystals according to claim 1 wherein the thin sheet contains at least one inactive substance selected from a carbonaceous substance, carbide, nitride, silicide and metallic oxide, as well as the secondary particles of calcium silicate crystals, fibrous material and coagulant.

PCT

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国際事務局

特許協力条約に基づいて公開された国際出願

<p>(51) 国際特許分類⁴ C04B 28/18, B28B 1/52 // (C04B 28:18, 14:02, 14:38 C04B 16:02, 16:04, 22:08 C04B 24:24)</p>	<p>A1</p>	<p>(11) 国際公開番号 606344 WO 88/09777</p> <p>(43) 国際公開日 1988年12月15日 (15.12.88)</p>
<p>(21) 国際出願番号 PCT/JP87/00383</p> <p>(22) 国際出願日 1987年6月12日 (12.06.87)</p> <p>(71) 出願人 (米国の除外を除くすべての指定国について) 株式会社大阪ペナック製造所 (KABUSHIKI KAISHA OSAKA PACKING SEIZOSHO) (JP/JP) 〒556 大阪府大阪市浪速区大國1丁目1番6号 Osaka, (JP)</p> <p>(72) 発明者: および</p> <p>(75) 発明者/出願人 (米国についてのみ) 井手 秀 (IDE, Tsutomu) (JP/JP) 〒501-05 岐阜県揖斐郡大野町大字公郎1110番地の69 Gifu, (JP) 濱田 博 (HAMADA, Suguru) (JP/JP) 〒502 岐阜県岐阜市長良長洞3484-7 Gifu, (JP)</p> <p>(74) 代理人 弁理士 三枝英二, 外 (SABGUSA, Eiji et al.) 〒541 大阪府大阪市東区平野町2丁目10番地 沢のビル Osaka, (JP)</p>	<p>(81) 指定国 AT (欧州特許), AU, BE (欧州特許), BR, CH (欧州特許), DE (欧州特許), FR (欧州特許), GB (欧州特許), IT (欧州特許), JP, LU (欧州特許), NL (欧州特許), SE (欧州特許), US.</p> <p>添付公開書類 国際調査報告書</p> <p>A.O.L.P. 9 MAR 1989</p> <div data-bbox="982 709 1266 871" style="border: 1px solid black; padding: 5px; text-align: center;"> <p>AUSTRALIAN - 4 JAN 1989 PATENT OFFICE</p> </div> <div data-bbox="917 924 1291 1060" style="border: 1px solid black; padding: 5px;"> <p>... is the amendment ... and Section 9 ... for printing</p> </div>	
<p>(54) Title: CALCIUM SILICATE CRYSTAL BOARD</p> <p>(54) 発明の名称 珪酸カルシウム結晶のボード</p> <p>(57) Abstract</p> <p>A calcium silicate crystal board which is formed of a plurality of thin layers of not more than 2 mm in thickness of each layer, with each layer containing secondary particles of calcium silicate crystals, a fibrous substance, and a coagulant adsorbed on the surfaces of the secondary particles for mutually binding the secondary particles to each other, and each layer being strongly bound to each other by the secondary particles of calcium silicate crystals present on the surfaces of the layers.</p>		

(57) 要約

珪酸カルシウム結晶の二次粒子を含有し、更に繊維質物質及び該二次粒子表面に吸着された凝集剤を含有し且つ上記二次粒子が相互に連結して形成される厚さ2 mm以下の薄葉体が複数枚積層されて形成され、上記積層された薄葉体相互がその表面部の珪酸カルシウム結晶二次粒子により強固に連結され一体化されていることを特徴とする珪酸カルシウム結晶のボード。

情報としての用途のみ

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SPECIFICATION

BOARDS OF CALCIUM SILICATE CRYSTALS

Field of the Invention

5 This invention relates to boards of calcium silicate crystals.

Background Art

Japanese Examined Patent Publication

10 No.40896/1973 discloses a board of calcium silicate crystals composed of secondary particles of xonotlite crystals and wood fibers. Said board is produced by forming a single layer of wet mat from an aqueous slurry of secondary particles of xonotlite crystals and wood fibers with use of a forming machine and press-molding the layer of wet mat with heating. The board of calcium silicate crystals obtained by such method is one press-molded from the single layer of wet mat and contains as the constituents the secondary particles of xonotlite crystals and wood fibers.

15 20 The board of calcium silicate crystals having the above construction is insufficient in the strength, particularly bending strength even if the board is composed predominantly of wood fibers or containing 50% or more thereof. This tendency is pronounced in the board
25 composed predominantly of calcium silicate crystals, more



specifically containing a small amount of wood fibers and 50% or more of calcium silicate crystals. In particular the board containing 80% or more of calcium silicate crystals has an unsatisfactory strength. On the other hand, the smaller the amount of wood fibers, the more preferable the board is in view of incombustibility. However, the aforesaid technique can not produce boards sufficient in both the incombustibility and satisfactorily great strength. Further the foregoing method essentially employs wood fibers for production of articles of great strength. The publication teaches nothing about the use of inorganic fibers without or in place of wood fibers. Among the boards thus produced, those of large thickness tend to have a bending strength reduced due to the irregularity of strength caused by the difference in the proportions of calcium silicate crystals and wood fibers between the internal and external board portions. Further this tendency becomes marked in boards having a thickness of 20 mm or more.

Disclosure of the Invention

An object of the present invention is to provide a board of calcium silicate crystals outstanding in mechanical strength, particularly bending strength.

Another object of the invention is to provide a board of calcium silicate crystals which contains a



predominant amount of calcium silicate crystals and a small amount of wood fibers or inorganic fibers in lieu of wood fibers and which is thus incombustible and excellent in mechanical strength.

5 A further object of the invention is to provide a board of calcium silicate crystals which even with a large thickness is homogenous throughout the interior and excellent in mechanical strength.

10 The board of calcium silicate crystals according to the present invention is characterized in that the board is composed of a plurality of laminated thin sheets, each of the thin sheets having a thickness of 2 mm or less, containing secondary particles of calcium silicate crystals, a fibrous material and a coagulant adsorbed on
15 the surface of the secondary particles, and being formed from the secondary particles interconnected with one another, and said superposed thin sheets being firmly united with one another into an integral body by the secondary particles of calcium silicate crystals present
20 on the surface of the sheets.

Our research revealed the following. In the board of calcium silicate crystals formed from secondary particles of calcium silicate crystals and a fibrous material, the secondary particles retain the coagulant as
25 adsorbed on the surface thereof and are interlocked with



one another to form thin sheets and the plurality of thin sheets as superposed are firmly interconnected by the secondary particles on the surface of sheets into an integral sheet. With this structure, the board exhibits a significantly great mechanical strength even if composed predominantly of calcium silicate crystals and displays a great mechanical strength even if containing 20% or less of wood fibers or synthetic or inorganic fibers instead of wood fibers, and the board even of large thickness has a uniformly great mechanical strength as a whole.

Furthermore, unlike conventional asbestos cement slates, the boards of calcium silicate crystals according to the present invention have the advantages of being low in specific gravity, excellent in strength and in fabrication property such as nailability and easy to pattern on the surface.

When each of the thin sheets constituting the board of the invention contains at least one inactive substance selected from a carbonaceous substance, carbide, nitride, silicide and metallic oxide, as well as the secondary particles of calcium silicate crystals, fibrous material and coagulant, a board is obtained which has an outstanding heat insulation properties over a wide temperature range, particularly a high temperature range. Consequently the inclusion of said inactive



substance in the board of the invention is among the preferred embodiments of the invention.

The secondary particles of calcium silicate crystals constituting the board of the invention are those of tobermorite crystals, xonotlite crystals and/or wollastonite crystals. Not only a single kind but two or more kinds of these crystals are usable. The secondary particles of calcium silicate crystals can be prepared, for example, by the methods disclosed in Japanese Examined Patent Publication No.12526/1978 and Japanese Unexamined Patent Publication No.146997/1978 in which a siliceous material and calcareous material are heated with stirring under an elevated pressure in an autoclave to undergo a hydrothermal synthesis reaction.

Examples of siliceous materials for producing the calcium silicate crystals are natural amorphous silicic acid, siliceous sand, silica gel, silica flour (such as ferrosilicon dust, etc.), white carbon, diatomaceous earth, silicas obtained by reacting aluminum hydroxide with hydrosilicofluoric acid produced as a by-product in the wet process for preparing phosphoric acid, and the like. Examples of useful calcareous materials include quick lime, slaked lime, carbide residuum, cement, etc. These siliceous and calcareous materials are usable singly or at least two of them can be used in mixture.



The CaO/SiO_2 mole ratio of the calcareous material to the siliceous material is about 0.7 to about 0.9 in synthesis of tobermorite crystals and about 0.90 to about 1.15 in synthesis of xonotlite crystals.

5 A starting slurry is prepared by adding water to the siliceous material and calcareous material. The amount of water used for producing a starting slurry is 5 times or more, preferably 10 to 50 times, the amount by weight of the solids of the starting slurry. The starting
10 slurry thus prepared is then subjected to a hydrothermal synthesis reaction with stirring. The reaction is conducted under a saturated aqueous vapor pressure of usually 4 kg/cm^2 or more, preferably 6 to 30 kg/cm^2 , usually for about 0.5 to about 20 hours, thereby producing
15 secondary particles of calcium silicate crystals. When further baked to about 1000°C , the xonotlite crystals obtained above by the hydrothermal synthesis reaction can be converted to β -wollastonite crystals without change of the shape (secondary particles).

20 Examples of fibrous materials to be used in the present invention include organic and inorganic fibrous materials. Exemplary of useful organic fibers are wood pulp, waste paper pulp, knots residuum, flax, fiber, rayon and like cellulosic fibers and polyamide, polyester, vinylon, polyolefin and like synthetic fibers.



Illustrative of useful inorganic fibers are rockwool, slag wool, glass fibers, silica fibers, ceramic fibers, carbonaceous fibers, inorganic whiskers, asbestos and the like. These fibrous materials are usable singly or at least two of them can be used in suitable mixture.

According to the present invention, boards of great strength can be produced by even the use of a small amount of fibrous material in mixture with a major amount of calcium silicate crystals. Consequently it is possible to obtain boards having a great strength and an outstanding incombustibility by use of a small amount of organic fibers. Noninflammable boards of great strength can be also produced by use of inorganic fibers alone without use of organic fibers. The content of fibrous material in the molded body is as low as 2 to 30% by weight. The boards of the invention composed predominantly of calcium silicate crystals exhibit an outstanding strength and can be produced with a high moldability. The content of fibrous material is preferably 2 to 20% by weight, more preferably 5 to 15% by weight.

Coagulants useful in the invention include, for example, cationic coagulants, anionic coagulants and nonionic coagulants. These coagulants are usable singly or at least two of them can be used in suitable mixture.



Particularly the conjoint use of cationic coagulant and anionic coagulant is preferred. The coagulant used in producing the board of the invention results in the improvement of filtering property, efficient molding and production of a board of great strength. Preferred coagulants are polymeric ones. Examples of useful cationic coagulants are polyethyleneimine, dialkylamine-epichlorohydrin polycondensate, polyamideamine-epichlorohydrin modified product, cationic polyacrylamide and like cationic polymeric coagulants. Also usable are cationic inorganic coagulants such as aluminum polychloride, aluminum sulfate, sodium aluminate, ferrous sulfate, ferric sulfate, ferric chloride and the like. Representative of useful anionic coagulants are ammonium polyacrylate, sodium polyacrylate and like polyacrylates and acrylamide-acrylic acid copolymer, etc. Exemplary of useful nonionic coagulants are polyacrylamide, polyethylene oxide and the like.

The content of coagulant in the molded body of the invention is 1.5% by weight or less, preferably 0.05 to 1.0% by weight, when a cationic, anionic or nonionic coagulant is used singly. When a cationic coagulant and an anionic or nonionic coagulant are conjointly used, about 0.05 to about 1.0% by weight of the cationic coagulant and about 0.01 to about 1.0% by weight of the



anionic or nonionic coagulant are employed, preferably in a total amount of less than about 1.5% by weight.

5 The coagulants used in the present invention can produce the contemplated effects presumably by the following reasons. A cationic, anionic or nonionic coagulant used singly is adsorbed on the surface of secondary particles of calcium silicate so that the secondary particles and the fibrous material are coagulated with one another by the adsorbed coagulant.

10 When a cationic coagulant and an anionic or nonionic coagulant are conjointly used, the cationic coagulant is caused to become adsorbed on the secondary particles of calcium silicate having a negative electric charge, giving a positive electric charge to the secondary particles with the result that the calcium silicate secondary particles are strongly united with one another by the anionic or nonionic coagulant, thereby improving the filtering property of solids in the slurry.

15

20 When required, the board of the invention may contain an inactive substance such as a carbonaceous substance, carbide, nitride, silicide, metallic oxide and the like to improve the heat insulation properties, particularly over a high temperature range. At least one of carbonaceous substance, carbide, nitride, silicide and

25 metallic oxide is used as said inactive substance.



Examples of useful inactive substances are carbonaceous substances such as active carbon, charcoal, coal, carbon black, graphite, etc.; carbides such as silicon carbide, boron carbide, titanium carbide, etc.; nitrides such as
5 silicon nitride, boron nitride, titanium nitride, etc.; silicides such as calcium silicide, etc.; and metallic oxides such as iron oxides (hematite, magnetite, etc.), titanium oxides (rutile, etc.), tin oxides, manganese oxides, zirconium oxides, ilmenite, zircon, chromite,
10 cerium oxides, lanthanum oxides, yttrium oxides, neodymium oxides, etc. These substances are usable singly or at least two of them can be used in mixture. It is suitable that the active substance be usually about 0.001 to about 120 μm , preferably 0.001 to 100 μm , in particle size.

15 The content of the inactive substance in the board of the invention can vary over a wide range and ranges usually from about 2 to about 70% by weight, preferably about 5 to about 50% by weight.

20 For producing the board of the invention, an aqueous slurry of secondary particles of calcium silicate crystals is prepared first. The aqueous slurry can be prepared by subjecting a calcareous material and siliceous material to a hydrothermal synthesis reaction as described hereinbefore, or by dispersing the secondary particles in
25 water. To the aqueous slurry are added a fibrous



material, a coagulant, and when required, an inactive substance. The amounts of these components used are accommodated to the desired contents thereof, calculated as the solids, in the board. The inactive substance may
5 be added to the starting slurry containing siliceous and calcareous materials prior to preparation of secondary particles of calcium silicate crystals, followed by a hydrothermal synthesis reaction of slurry. Thereby the inactive substance is united with the secondary particles
10 of calcium silicate crystals, resulting in an increase in the strength of the board.

Then thin sheets are formed from an aqueous slurry which contains secondary particles of calcium silicate crystals, a fibrous material, a coagulant and when required, an inactive substance. In formation of thin sheets, it is desirable to adjust the solids concentration of slurry to about 0.2 to about 3% by weight.

Thin sheets are formed by any of continuous methods (cylinder-type, Fourdrinier-type, short wire-type or the like) and batchwise methods (CTC method, Chapman method or the like). A plurality of thin sheets thus
20 formed are superposed over one another into a laminate sheet. Preferably the laminate sheet is then cut by a cutter as required and press-molded to a predetermined
25 thickness with a hot press or the like with heating while



being dried. A suitable heating temperature is about 150 to about 200°C and an adequate molding pressure is about 10 to about 50 kg/cm².

In the laminate sheet thus obtained by press-
molding of thin sheets with heating, the secondary
particles of calcium silicate crystals in each thin sheet
are interlocked with one another so that each thin sheet
is strengthened and the secondary particles of calcium
silicate crystals on the surface of each thin sheet are
interconnected with one another, giving a board of great
strength in which the thin sheets are firmly united with
one another. The board of the invention as observed in
cross section under an optical microscope (at a
magnification of 70 X) shows that the layers are
integrally united with one another by the secondary
particles of calcium silicate crystals and that the
boundaries between the layers can not be microscopically
recognized.

The thin sheets constituting the board of the
invention each has a thickness of about 2 mm or less,
preferably about 0.2 to about 1.0 mm. The board of the
invention is comprised of a plurality of thin sheets, more
specifically 3 to 200 thin sheets, which are formed into
an integral sheet. The board of the invention even with a
large thickness has a high bending strength which is



uniform therethrough. Thus it is possible to obtain a board 20 mm or more in thickness and great in the strength.

Examples

5 The present invention is described below in greater detail with reference to the following Preparation Example and Examples in which the parts and the percentages are all by weight unless otherwise specified.

Preparation Example

10 A starting slurry was prepared by adding 49 parts of lime slaked with hot water at about 85°C and 51 parts of silica stone powder (CaO/SiO_2 mole ratio of 1.0) to water in 12 times the amount of the solids. The starting slurry was subjected with stirring to a
15 hydrothermal synthesis reaction under a pressure of 15 kg/cm^2 with stirring for 4 hours, giving an aqueous slurry of secondary particles of xonotlite crystals.

Example 1

20 The secondary particles of xonotlite crystals and fibers were mixed in specific proportions, and the mixture was adjusted with water to a concentration of 2.0%. The mixture was mixed with 0.1% of a cationic coagulant, "Polymaster R607" (product of Hakuto Chemical Co., Ltd., dimethylamine-epichlorohydrin polycondensate)
25 and a specific amount of an anionic coagulant, "Polymaster



R623S" (product of Hakuto Chemical Co., Ltd.,
polyacrylamide-polyacrylic acid copolymer), producing a
starting slurry.

5 The thus obtained starting slurry was formed
into green thin sheets of 0.7 mm thickness with use of a
short wire-type forming device. Thirty green thin sheets
thus formed were superposed over one another and press-
molded with heating at 185°C with a hot press to produce a
9 mm-thick molded board of calcium silicate.

10 Table 1 shows the amounts of components and
properties of the molded boards.





- 15 -

Specimen No.	1	2	3	4	5
Amount (part by weight)					
Xonotlite secondary particles	79.7	84.7	89.7	89.7	95.7
Pulp (NEKP)	20	15	8		
Glass fibers			2	2	4
Ceramic fibers				8	
Cationic coagulant (Polymaster R-607)	0.1	0.1	0.1	0.1	0.1
Anionic coagulant (Polymaster R-623S)	0.2	0.2	0.2	0.2	0.2
Properties of molded product					
Thickness of molded product (mm)	9	9	9	9	9
Number of laminated sheets (sheet)	30	30	30	30	30
Density (g/cm ³)	0.639	0.631	0.628	0.624	0.630
Bending strength (kg/cm ²)	161	149	140	125	105
Thermal linear shrinkage percentage (%)	1.72	1.44	1.17	1.00	1.17
Incombustibility	Almost incom- bustible	Incom- bustible	Incom- bustible	Incom- bustible	Incom- bustible
Fabrication property	Good	Good	Good	Good	Good

A 4x4 grid of dots forming a stylized letter 'A'. The dots are arranged as follows (row by row):
 Row 1: (1,1), (1,2), (1,3), (1,4)
 Row 2: (2,1), (2,2), (2,3), (2,4)
 Row 3: (3,1), (3,2), (3,3), (3,4)
 Row 4: (4,1), (4,2), (4,3), (4,4)

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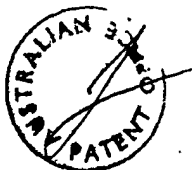
- According to Notice No.1828 of Ministry of
Construction, Japan.

- Among the molded products tested by e.g., nailing and sawing, those which neither developed any crack nor chipped at any edge were rated good.

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20

25



determined.

Ninety green thin sheets of about 1 mm thickness thus obtained were superposed over one another and press-molded in the same manner as in Example 1, producing a 40
5 mm-thick molded board of calcium silicate.

The amounts of components and properties of the molded boards were shown in Table 2.

Table 2 also shows, for comparison, the properties of molded board produced in the same manner as
10 above without use of a coagulant under the column of comparison example.





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Table 2

Specimen No.	1	2	3	4	5	Comp. Ex.
Proportions of components (%)						
Xonolite secondary particles	89.7	89.7	89.7	89.7	89.7	90
Pulp	8	8	8	8	8	8
Glass fibers	2	2	2	2	2	2
Cationic coagulant						
Polymaster R-607	0.1	0.1				
Aronflock C-325			0.3			
Anionic coagulant						
Polymaster R-623S	0.2			0.3		
Nonionic coagulant						
Polymaster R-620		0.2			0.3	



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Table 2 (continued)

Specimen No.	1	2	3	4	5	Comp.Ex.
Properties of molded product						
Thickness of molded product (mm)	40	40	40	40	40	40
Number of laminated sheets (number)	90	90	90	90	90	90
Density of molded product (g/cm^3)	0.625	0.632	0.635	0.629	0.630	0.584
Bending strength of molded product (kg/cm^2)	135	131	120	119	116	65
Thermal linear shrinkage percentage (%)	1.21	1.21	1.17	1.30	1.17	1.17
Incombustibility	Incom- bustible	Incom- bustible	Incom- bustible	Incom- bustible	Incom- bustible	Incom- bustible
Fabrication quality	Good	Good	Good	Good	Good	-

Example 3

A starting slurry for forming green thin sheets was prepared by the same method as in Example 1 and was made into green thin sheets of about 0.7 mm thickness by a short wire-type forming device. The green thin sheets thus obtained were wound up under a pressure by a making roll and spread out to obtain a sheet-like body of 17.5 mm thickness. Four sheet-like bodies were superposed and press-molded with a hot press with heating at 185°C, producing a 60-mm thick molded board of calcium silicate.

Table 3 shows the amounts of components and properties of the molded board,



Table 3

Specimen No.	1
Proportions of Components (%)	
Xonotlite secondary particles	89.7
Pulp (NBKP)	8.0
Glass fibers (Ceramic fibers)	2.0
Cationic coagulant (Polymaster R-607)	0.1
Anionic coagulant (Polymaster R-623S)	0.2
Sheets formed by making roll	
Thickness (mm)	17.5
Number of laminated sheets (number)	45
Water content (%)	211
Properties of molded product	
Thickness (mm)	60
Number of laminated sheets (number)	4
Density (g/cm ³)	0.554
Bending strength (kg/cm ²)	115
Thermal linear shrinkage percentage (%)	1.27
Incombustibility	Incombustible
Fabrication property	Good



Example 4

Quick lime (CaO 95%) was slaked in hot water at 80°C to produce a milk of lime. To the milk of lime was added a powder of silica stone (SiO₂ 94%), 7.1 μm in mean particle size, in the CaO/SiO₂ mole ratio of 1.00. Further added were water and a predetermined amount of a powder of titanium oxide (rutile, 1.2 μm in mean particle size) in such an amount that the total amount of water was 12 times the amount of the solids. In this way, a starting slurry was prepared.

The starting slurry was placed into an autoclave under a saturated vapor pressure of 12 kg/cm² at 191°C and subjected to a hydrothermal synthesis reaction for 6 hours while being stirred by a stirrer which was rotated at 40 r.p.m. In this way, crystal slurries were produced.

Portions of the crystal slurries obtained above were dried for 24 hours at 100°C and analyzed by X-ray diffractometer. The analysis revealed the peak of xonotlite crystals in all specimens and further the peak of rutile crystals in the specimens containing titanium oxide particles.

Subsequently, 8% of pulp and 2 % of glass fibers were mixed with each of the crystal slurries, and water was added to the mixture to a concentration of 2.0% in the slurry. Further added was a cationic coagulant



(Polymaster R-607, product of Hakuto Chemical Co., Ltd.)
in an amount of 0.1 % based on the slurry solids and then
an anionic coagulant (Polymaster R-623S) (product of
Hakuto Chemical Co., Ltd.) in an amount of 0.2 % based on
5 the slurry solids.

Thereafter each slurry thus obtained was
adjusted with water to a concentration of 1.0 % and made
into green thin sheets of about 0.7 mm thickness with use
of a short wire-type forming device. Ninety green thin
10 sheets thus prepared were superposed and press-molded with
a hot press to produce a 40 mm-thick molded board of
calcium silicate crystals. The properties of each molded
boards were determined according to the method of JIS A
9510 with the results shown below in Table 4.



Table 4

Specimen No.	1	2	3
In molded product (%)			
Xonotlite secondary particles	90	69.7	49.7
Rutile	0	20	40
Pulp (NBKP)	8	8	8
Glass fibers	2	2	2
Moldability	Good	Good	Good
Properties of molded product			
Thickness (mm)	40	40	40
Number of laminated sheets (number)	90	90	90
Density (g/cm ³)	0.403	0.404	0.406
Bending strength (g/cm ²)	65.2	49.3	42.8
Thermal linear shrinkage percentage (%)	1.20	1.19	1.22
Thermal conductivity (Kcal/m.h.°C)			
70°C	0.063	0.056	0.052
150°C	0.071	0.061	0.054
250°C	0.082	0.067	0.056
350°C	0.094	0.073	0.058

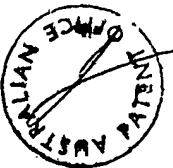


Example 5

Slurries of xonotlite crystals were produced by repeating the same procedure as in Example 4 with the exception of not adding titanium oxide particles.

5 To portions of the slurries was added the specific inorganic substance in such an amount that the molded product contains 25% of inorganic substance, and the slurry was molded in the same manner as in Example 1, producing a 25 mm-thick molded board of calcium silicate
10 crystals (The molded board consists of 64.7% of secondary particles of xonotlite crystals, 25% of inactive substance, 8% of pulp, 2% of glass fibers, 0.1% of cationic coagulant and 0.2% of anionic coagulant).

15 Table 5 shows the properties of the molded products obtained above.





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Table 5

Specimen No.	4	5	6	7
Inactive substance				
Kind	Silicon carbide	Iron oxide (Hematite)	Ilmenite	Manganese oxide
Content in molded product (%)	25	25	25	25
Mean particle size (μm)	3.5	0.8	5.4	4.0
Properties of molded product				
Bulk density (g/cm^3)	0.410	0.408	0.400	0.408
Bending strength (kg/cm^2)	45.3	44.2	45.1	46.7
Thermal conductivity ($\text{Kcal}/\text{m.h.}^\circ\text{C}$)				
Average temperature ($^\circ\text{C}$)				
70	0.056	0.056	0.057	0.055
150	0.059	0.059	0.059	0.058
250	0.064	0.064	0.065	0.064
350	0.071	0.072	0.075	0.071



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Table 5 (continued)

Specimen No.		8	9	10
Inactive substance				
Kind		Silicon nitride	Cerium oxide	Titanium oxide (Rutile)
Content in molded product (%)		25	25	25
Mean particle size (μm)		5.0	1.8	1.2
Properties of molded product				
Bulk density (g/cm^3)		0.411	0.405	0.409
Bending strength (kg/cm^2)		44.1	45.0	44.3
Thermal conductivity ($\text{Kcal}/\text{m.h.}^\circ\text{C}$)				
Average temperature ($^\circ\text{C}$)				
70		0.056	0.057	0.055
150		0.059	0.059	0.058
250		0.064	0.065	0.063
350		0.071	0.075	0.070

CLAIMS:

5 1. A board of calcium silicate crystals,
characterized in that the board is composed of a plurality
of laminated thin sheets, each of the thin sheets having a
thickness of 2 mm or less, containing secondary particles
of calcium silicate crystals, a fibrous material and a
coagulant adsorbed on the surface of the secondary
particles, and being formed from the secondary particles
interconnected with one another, and said superposed thin
10 sheets being firmly united with one another into an
integral body by the secondary particles of calcium
silicate crystals present on the surface of the sheets.

15 2. A board of calcium silicate crystals
according to claim 1 wherein the calcium silicate crystals
are tobermorite crystals, xonotlite crystals and/or
wollastonite crystals.

20 3. A board of calcium silicate crystals
according to claim 1 wherein the coagulant is a polymeric
one.

4. A board of calcium silicate crystals
according to claim 3 wherein the polymeric coagulant is a
cationic coagulant and an anionic coagulant or a nonionic
coagulant.

25 5. A board of calcium silicate crystals
according to claim 1 wherein the content of fibrous



material is 2 to 30% by weight.

6. A board of calcium silicate crystals according to claim 5 wherein the content of fibrous material is 2 to 20% by weight.

5 7. A board of calcium silicate crystals according to claim 5 wherein the content of fibrous material is 5 to 15% by weight.

8. A board of calcium silicate crystals according to claim 1 wherein the thin sheet contains at
10 least one inactive substance selected from a carbonaceous substance, carbide, nitride, silicide and metallic oxide, as well as the secondary particles of calcium silicate crystals, fibrous material and coagulant.

9. A board of calcium silicate crystals
15 according to claim 8 which contains 2 to 70% by weight of the inactive substance.

10. A board of calcium silicate crystals according to claim 8 wherein the carbonaceous substance is at least one of active carbon, charcoal, coal, carbon
20 black and graphite; the carbide is at least one of silicon carbide, boron carbide and titanium carbide; the nitride is at least one of silicon nitride, boron nitride and titanium nitride; the silicide is calcium silicide; and the metallic oxide is at least one of iron oxides,
25 titanium oxides, tin oxides, manganese oxides, zirconium



oxides, ilmenite, zircon, chromite, cerium oxides,
lanthanum oxides, yttrium oxides and neodymium oxides.

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INTERNATIONAL SEARCH REPORT

International Application No **PCT/JP87/00383**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl⁴ C04B28/18, B28B1/52// (C04B28/18, C04B14/02, C04B14/38, C04B16/02, C04B16/04, C04B22/08, C04B24/24)		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC	C04B28/18, C04B14/38, C04B16/04, B28B1/52	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
Jitsuyo Shinan Koho		1926 - 1986
Kokai Jitsuyo Shinan Koho		1971 - 1986
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	JP, A, 61-83667 (Nichiasu Kabushiki Kaisha) 28 April 1986 (28. 04. 86) Page 2, right column, lower part, line 3 to page 3, right column, lower part, line 16 (Family: none)	1-10
Y	JP, A, 59-91009 (Matsushita Electric Works, Ltd.) 25 May 1984 (25. 05. 84) Page 2, right column, lower part, 6th line from the bottom to first line (Family: none)	1-10
Y	JP, A, 52-105926 (Nippon Asbestos Co., Ltd.) 6 September 1977 (06. 09. 77) Page 2, right column, upper part, line 14 to page 3, left column, upper part, line 6 (Family: none)	1-10
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁶</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"S" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *		Date of Mailing of this International Search Report *
August 4, 1987 (04. 08. 87)		August 24, 1987 (24. 08. 87)
International Searching Authority ¹		Signature of Authorized Officer ¹⁹
Japanese Patent Office		

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 52-135330 (Nippon Asbestos Co., Ltd.) 12 November 1977 (12. 11. 77) Page 2, right column, lower part, line 4 to page 3, right column, lower part, line 15 & GB, A, 1,532,612 & US, A, 4,144,121 & JP, B4, 55-049023	1-10
Y	JP, B4, 53-012526 (Kabushiki Kaisha Osaka Packing Seizosho) 1 May 1978 (01. 05. 78) Column 3, line 17 to column 5, line 35 (Family: none)	2

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹⁰ not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹⁰, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 53-146997 (Kabushiki Kaisha Osaka Packing Seizosho) 17 August 1977 (17. 08. 77) Page 3, right column, lower part, line 9 to page 5, left column, lower part, last line & DE, A1, 2705828 & BR, A, 7700875 & AU, A1, 2215477	2
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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers, because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.